Kinetics and Mechanism of the Bromination of 2,4-Dihydroxy Benzoic Acid

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ABSTRACT

Kinetics of the bromination of 2,4-dihydroxy benzoic acid in aqueous solution by bromine has been studied potentiometrically. The rate shows second order kinetics i.e. first order with respect to 2, 4-dihydroxy benzoic acid and bromine. A suitable mechanism in conformity with the kinetic observations has been proposed. Various activation parameters such as frequency factor, energy of activation and entropy of activation are calculated from kinetic measurements.

Keywords: Kinetics, Bromination, 2, 4-dihydroxy benzoic acid, Steady state Principle.

INTRODUCTION

Introduction of bromine into organic molecules is an important and fundamental reaction in organic chemistry, owing to the considerable commercial importance of such compounds. They can be used as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidising agents and also an industrial intermediates in the manufacture of pharmaceuticals, agrochemicals and other specially products, for instance flame retardants.[2,6,7,8,10.] Electrophilic aromatic bromination is an important reaction known to organic chemist.

Brominated aromatic compounds are paramount importance as building block in organic synthesis. They play key role in preparation of organometatallic reagents [4,5] and vital roles in transition metal mediated coupling reactions.[1,3,9.]

In present study bromination of 2,4-Dihydroxy benzoic acid has been carried out. The reaction is too rapid to be studied by conventional techniques. Hence the bromination has been carried out by steady state technique. The kinetic and

thermodynamic parameters are evaluated. A plausible mechanism for the reaction has been proposed.

EXPERIMENTAL

The stock solutions of 1.0×10^{-1} M allyl alcohol, 0.5 M sulphuric acid, 1.0×10^{-2} M 2,4-dihydroxy benzoic acid, 1.0×10^{-2} M potassium bromide, 1.0×10^{-2} M potassium bromate were prepared. The study of the kinetics of bromination of 2,4-dihydroxy benzoic acid is carried out in different parts:

1. Measurement of rate of production of bromine

Appropriate amount of allyl alcohol, sulphuric acid and potassium bromate were mixed together and were diluted to 250 cm^3 (Solution A). The required amount of potassium bromide was also diluted to 250 cm^3 (Solution B). 10.0 cm^3 each of solution A and solution B were taken in two different beakers and maintained in a thermostat at 25.0°C. After they had attained the thermostat temperature, the solutions were mixed quickly in a beaker kept in thermostat and simultaneously a stop-watch was started. The initial concentrations of the reactants in the mixture were 1×10^{-4} M allyl alcohol, 0.15 M sulphuric acid, 7.5×10^{-3} M potassium bromide and 1.5×10^{-3} M potassium bromate. A platinum foil electrode and saturated calomel electrode were introduced into the reaction mixture and the EMF was measured at the intervals of 25 seconds using electronic voltmeter. The measurements were continued till there was abrupt increase in the EMF values. The plot of EMF versus time was plotted and the time lapsed during inflexion point was the time required for complete bromination of allyl alcohol. The experiment was repeated to check the reproducibility and it was found that the results were in good agreement with one another within the limits of ± 2.0 seconds. From the results the rate of production of bromine can be evaluated (Table 1 and Fig. 1).

2. Measurement of redox potential of bromine under steady state condition

The procedure adopted in (1) was repeated here, the only difference being that the allyl alcohol was replaced by 2,4-Dihydroxy benzoic acid. The EMF measurements were carried out using the same electrode system. The measurements were made at intervals of 25 seconds. From EMF values the redox potential of bromine could be evaluated. Having evaluated the redox potential of bromine, the steady state concentration of bromine and hence specific reaction rate of the bromination of 2, 4-Dihydroxy benzoic acid could be determined, as explained in the results and discussion. (Table 2 and Fig. 2)

3. Determination of the order of reaction

To determine the order of the reaction, the earlier described procedure was repeated by varying the rate of production of bromine and changing the concentration of 2,4-Dihydroxy benzoic acid from 1.0×10^{-4} M to 2.0×10^{-4} M, from the results the order of reaction was deduced. (Table 3)

4. Determination of activation parameters

The specific reaction rate determination by procedure described in 1 and 2 was repeated at various temperature in the range of 20.0°C to 40.0°C (Table 3) and from the results the activation parameters such as energy of activation, frequency factor and entropy of activation were evaluated. (Table 4)

Table-1
Kinetics of the Bromination of 2,4-Dihydroxy Benzoic Acid: Rate of Generation of Bromine

Concentration of potassium bromide : 7.5×10^{-3} M; Concentration of potassium bromate:1.5×10^{-3} M; Concentration of sulphuric acid: 0.15 M; Concentration of allyl alcohol: 1.0×10^{-4}M; Temperature : 25 ºC

Time/S	EMF/mV	Time/S	EMF/mV
25	0.670	200	----
50	0.675	225	0.825
75	0.680	250	0.840
100	0.685	275	0.845
125	0.690	300	0.850
150	0.700	325	0.855
175	------		

Time to reach inflexion point = 197 S
Rate of production of bromine = 5.08×10^{-7} M S^{-1}

Table-4
Kinetics of the Bromination of 2,4-Dihydroxy Benzoic Acid

[KBr] = 7.5×10^{-3} M, [$KBrO_3$] = 1.5×10^{-3} M, [H_2SO_4] = 0.15 M, [2, 4-DIHYDROXY BENZOIC ACID] = 1.0×10^{-4} M; Temperature 25 ºC

Frequency factor, A	=	1.51×10^{15} $M^{-1}S^{-1}$
Energy of activation, Ea	=	27.8 KJ $Mole^{-1}$
Entropy of activation, ΔS^*	=	-37.41 JK^{-1} $Mole^{-1}$

Table-2

Kinetics of the Bromination of 2,4-Dihydroxy Benzoic Acid by Bromine

Concentration of potassium bromide : 7.5×10^{-3} M; Concentration of potassium bromate:1.5×10^{-3} M; Concentration of sulphuric acid: 0.15 M; Concentration of 2,4-Dihydroxy benzoic acid: 1.0×10^{-4}M; Temperature : 25 ºC

Time/S	EMF/V
(Extrapolated)	0.605
25	0.620
50	0.625
75	0.635
100	0.640
125	0.650
150	0.670
175	0.675
200	0.690
225	0.700
250	0.710

Extrapolated value of EMF = 0.605 V
Specific reaction rate, k_2 = 20.3×10^9 M^{-1} S^{-1}

Table-3
Kinetics of the Bromination of 2,4-Dihydroxy Benzoic acid: Effect of Temperature

Concentration of potassium bromide : 7.5×10^{-3} M; Concentration of potassium bromate: 1.5×10^{-3} M; Concentration of sulphuric acid: 0.15 M; Concentration of 2,4-Dihydroxy benzoic acid: 1.0×10^{-4}M

Temp / °C	Temp, T/K	$\frac{1}{T}$ / 10^{-3} K^{-1}	k_2 / 10^9 $M^{-1}S^{-1}$	log k_2
20	293	3.413	14.1	10.149
25	298	3.356	20.3	10.307
30	303	3.300	23.3	10.367
35	308	3.247	26.7	10.427
40	313	3.195	32.8	10.516

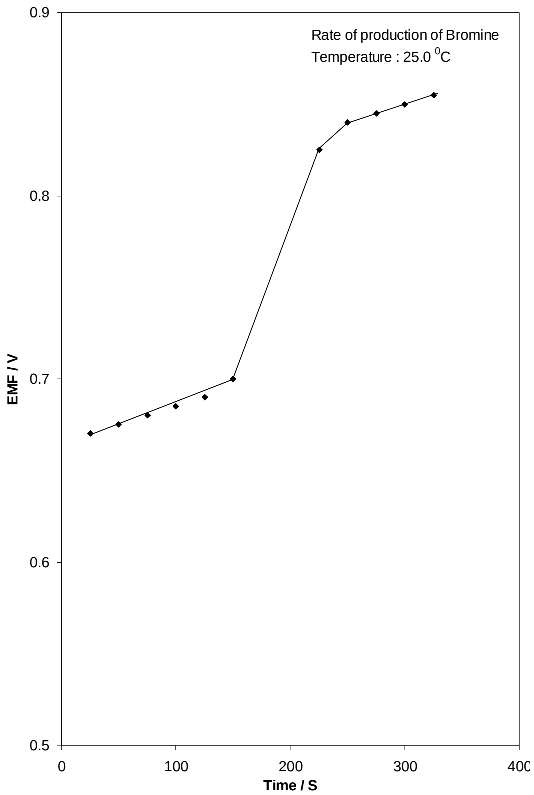


Fig. 1: Kinetics of the bromination of 2,4-dihydroxy benzoic acid

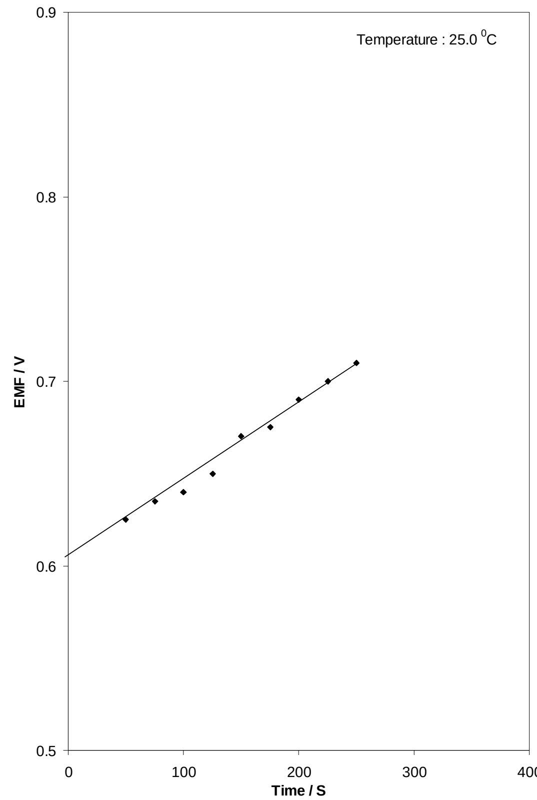


Fig. 2: Kinetics of the bromination of 2,4-dihydroxy benzoic acid

RESULTS AND DISCUSSION

A plot of EMF versus time was drawn (Fig. 1). The plot consisted of an initial linear portion corresponding to the steady state, then a sudden increase in EMF indicating complete bromination of the allyl alcohol and lastly a gradual increase in EMF due to accumulation of bromine. The point of inflexion in the curve gave the instant when the bromination was completed and from this point the time required for the complete bromination of allyl alcohol was evaluated at 25.0°C. In this reaction 1mole of allyl alcohol requires 1 mole of bromine. Therefore the rate of production of bromine $(\text{Rate})_{\text{prod.}}$ is obtained by the ratio of concentration of allyl alcohol to the time of inflexion. The steady state concentration of bromine for the bromination of 2,4-Dihydroxy benzoic acid at 25.0°C can be evaluated from Nernst equation and is given by the equation, $E = 0.978 + 0.0296 \log[Br_2]$.

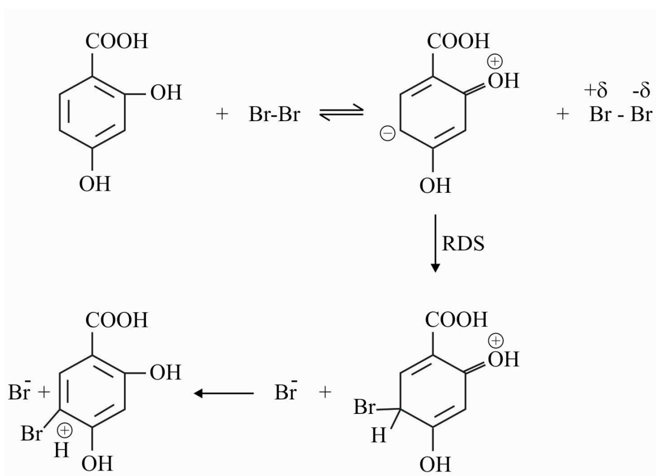
This potential is due to steady state concentration of bromine at zero time. For the evaluation of this potential, at 25.0 °C a plot of EMF versus time was plotted and extrapolated to zero time (Fig. 2). By putting

the extrapolated value in the above equation, concentration of bromine can be evaluated. At steady state,

$(Rate)_{prod}$ = k_2 [2,4-Dihydroxy benzoic acid] $[Br_2]$

$$\therefore k_2 = \frac{(Rate)_{prod}}{[2,4\text{-Dihydroxy benozoic acid}][Br_2]}$$

It was observed that by varying the rate of production of bromine and changing the concentration of 2,4-Dihydroxy benzoic acid from 1.0×10^{-4} M to 2.0×10^{-4} M, the specific reaction rate, k_2, almost remains unaltered. Therefore, the bromination of 2,4-Dihydroxy benzoic acid by bromine is a second order reaction. The specific reaction rates were evaluated at various temperatures in the range of 20.0°C to 40.0°C. The plot of log k_2 versus 1/T gives a straight line. From slope of the plot, the energy of activation is calculated. The value of other activation parameters such as frequency factor, A, entropy of activation, (ΔS*) are also calculated. The bromate-bromide reaction in acid medium produce bromine in molecular form or in hydrolysed form but the molecular bromine is the reacting species in the bromination of 2,4-Dihydroxy benzoic acid. Therefore the accepted machanism for the bromination reaction is



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